Quantum Chemical Study on Molecular and Electronic Structures of Methyl and Methoxyl Substituted Cu(II) and Ni(II) Benzoic Acid Hydrazides Ions

I. O. ADEOYE, O. A. ODUNOLA, M. A. OLADIPO and B. SEMIRE

Department of Pure and Applied Chemistry,
Ladoke Akintola University of Technology,
P.M.B 4000 Ogbomosho, Nigeria.
odunola@yahoo.com

Received 30 August 2007; Accepted 20 October 2007

Abstract: The electronic structures of model methyl and methoxyl substituted benzoic acid hydrazides of Ni(II) and Cu(II) complexes have been studied both at semi empirical level (PM3). The *ortho*-methoxyl is relatively stable which may be due to the formation of hydrogen bonds between methoxyl oxygen and hydrogen on hydrazide ($\text{CH}_3\text{O} \cdots \text{HNNH}$; 1.817 Å for Cu(II) and 1.806~1.839 Å for Ni(II)). The change in torsion in the complexes affect π -electrons delocalization (complexes containing π -electrons system) and consequently affect the band gap which is a measure of electronic properties that control the reactivity of the complexes. The curves for *ortho* and *para* methoxyl substituted Cu(II) complexes intercept at 50° and 135°-144°, this could suggest that both complex ions can co-exist and react in very similar ways in solution under certain conditions.

Keywords: Substituent effect, Electronic structure, Benzoic acid hydrazides, Semi empirical, PM3.

Introduction

The $-\text{CONHNH}_2$ moiety of hydrazides have attracted considerable interest in the literature partly because of their coordinating ability to chelate a variety of transition metal ions¹⁻² and their importance of organic chemistry since they are included in retro-bispeptides³⁻⁵ which are used to design enzyme substrate mimics and potential inhibitors and in aliphatic polyamides⁶⁻⁹ which display structures different to the extended conventional ones. However the number of studies about molecular and electronic structures of the hydrazides moiety is scarce¹⁰. There has been investigation into conformational preferences of hydrazide functional

groups in both gas phase and aqueous solution using *ab-initio* quantum mechanical calculations¹¹. Recently a number of tin complexes were studied and in any case they seem to manifest efficient anticancer activity^{12,13}. The advantage of their use as antitumour medicine lies in their lower costs and possibly in a greater effectiveness. However, in general, a satisfactory understanding of the mode of action of the drug requires a thorough study of its interaction with the relevant biomolecules or their model systems¹⁴.

Hydrazides generally have also shown a lot of promising biological activity, which could easily lead to their adaptation as a drug. In this paper, the electronic structures and stabilities of substituted Copper(II) and Nickel(II) benzoic acid hydrazides ions were studied using semi empirical method (PM3) (Figure 1).

Figure 1. Sketch structures of M(II) benzoic acid hydrazides ions [a=Copper(II), b=Nickel(II) and X = methyl or Methoxyl].

Computational details

The unsubstituted and substituted $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$ and $\text{Ni}[\text{C}_6\text{H}_7\text{CON}_2]_3^{2+}$ complexes were modeled using Spartan 04 essential¹⁵. The structures were fully optimized¹⁶ at the PM3. PM3 method is a computational efficient technique that gives conformation and heats of formation in qualitative good agreement with trend in results of more accurate methods¹⁷.

Results and Discussion

Stability and geometry

Table 1 shows the heats of formation of the two series of Cu(II) and Ni(II) benzoic acid hydrazides ions. The stability of the Cu(II) complex ions increases in the order *ortho* < *meta* < *para* for methyl substituted. However, in methoxyl substituted Cu(II) complex ions, the stability increases in the order *meta* < *ortho* < *para* (the *ortho* methoxyl substituted is more stable than the *meta* substituted). In Ni(II) hydrazide ions, *meta*-methyl substituted is most stable and *ortho*-methoxyl substituted is energetically preferred, it is more stable than *para*-methoxyl substituted. The relative stability of methoxyl may be due to the formation of Hydrogen bonds between methoxyl oxygen and hydrogen on hydrazide ($\text{CH}_3\text{O} \cdots \text{HNNH}$; 1.817Å for Cu(II) and 1.806~1.839Å for Ni(II)) as shown in Figure 2.

Table 1. Heats of formation (kcal/mol) and HOMO-LUMO energy difference (eV) as calculated using PM3.

Substitution	Heats of formation, kcal/mol		E _{HOMO-LUMO} , eV	
	Cu[C ₆ H ₇ CON ₂] ₂ ²⁺	Ni[C ₆ H ₇ CON ₂] ₃ ²⁺	Cu[C ₆ H ₇ CON ₂] ₂ ²⁺	Ni[C ₆ H ₇ CON ₂] ₃ ²⁺
Un-sub.	330.959	-140.982	7.711	7.323
<i>o</i> -CH ₃	311.268	-136.143	6.331	5.711
<i>m</i> -CH ₃	304.891	-171.014	6.158	6.935
<i>p</i> -CH ₃	301.187	-171.725	6.280	6.965
<i>o</i> -OCH ₃	240.757	-268.942	7.493	7.238
<i>m</i> -OCH ₃	255.567	-232.267	5.113	5.650
<i>p</i> -OCH ₃	236.457	-262.875	6.094	6.650

Figure 2. *Ortho*-methoxyl substituted showing hydrogen bonds, (a) *ortho*-methoxyl Ni[C₆H₇CON₂]₃²⁺ and (b) *ortho*-methoxyl Cu[C₆H₇CON₂]₂²⁺.

The trends in stability of these series of complex ions coincide with that of HOMO-LUMO gaps (Δ); the higher the stability the larger the Δ gaps. Table 2 shows selected bond lengths and bond angles of the complexes calculated at PM3 level. The bond lengths of Cu(II) hydrazides are more or less affected with methyl substitution but methoxyl substitution affects bond lengths by shortened Cu-O and lengthened Cu-N especially for *ortho*- and *para*-substitutions. Both methyl and methoxyl substitutions affect copper-hydrazides bond angles ($\angle$ CuN1N2 and CuN3N4) as compared to un-substituted. In case of Ni(II) hydrazides, greater distortion is noticed in both methyl (except *m*-CH₃) and methoxyl substitutions as reflected in bond lengths and bond angles ($\angle$ NiN1N3, NiN2N4 and NiN5N6).

Torsion potentials

The Torsion potential curves for Ni[C₆H₇CON₂]₃²⁺ and Cu[C₆H₇CON₂]₂²⁺ and their substituted derivatives associated with the rotation of the one of CNNC in different directions are shown in Figures 3, 4, 5 and 6. The energy barrier high for the un-substituted and methyl substituted Ni[C₆H₇CON₂]₃²⁺ (Figure 3) is less than 1.0 kcal/mol (almost flat). This shows that position (*ortho*, *meta* or *para*) of the methyl substituent is the major determining factor to the stability of the complexes rather than the methyl; this may be due to internal rotation restriction of the complex ions. In the methoxyl substituted Ni complexes, the energy barrier experienced is not similar to that of methyl-substituted, except in *ortho*-methoxyl position. The energy barrier experienced in *m*-OCH₃ substituted is about 4.0 kcal/mol, therefore there would be a greater internal rotation in *m*-OCH₃ substituted as compared to other methoxyl positions, which may have substantial influence on the chemical reactivity of the complex (Figure 4).

Table 2. Selected bond lengths (Å) and bond angles (°) for Ni(II) and Cu(II) hydrazides derivatives.

Cu(II) Complexes							
Bond length	Un-sub.	<i>O</i> -CH ₃	<i>m</i> -CH ₃	<i>p</i> -CH ₃	<i>o</i> -OCH ₃	<i>m</i> -OCH ₃	<i>p</i> -OCH ₃
Cu-O1	1.849	1.832	1.832	1.832	1.848	1.844	1.842
Cu-O2	1.840	1.846	1.846	1.846	1.848	1.839	1.833
Cu-N1	1.834	1.847	1.847	1.847	1.834	1.855	1.843
Cu-N2	1.834	1.842	1.842	1.842	1.834	1.859	1.847
<CuN1N3	105.05	106.34	106.51	106.51	105.01	101.97	103.14
<CuN2N4	105.05	103.58	103.55	103.55	105.01	102.33	106.84
<CuO1C1	108.30	108.99	108.99	108.99	108.20	106.45	108.22
<CuO2C2	108.30	106.34	108.32	108.32	108.20	107.89	108.96
Ni(II) Complexes							
Ni-O1	1.875	1.870	1.875	1.851	1.850	1.870	1.850
Ni-O2	1.862	1.866	1.862	1.862	1.894	1.867	1.840
Ni-O3	1.839	1.852	1.839	1.840	1.852	1.853	1.860
Ni-N1	1.882	1.867	1.882	1.896	1.874	1.866	1.896
Ni-N2	1.872	1.884	1.872	1.893	1.883	1.885	1.893
Ni-N3	1.871	1.852	1.871	1.846	1.862	1.854	1.846
<NiN1N3	105.41	105.70	105.42	101.09	105.85	105.75	100.99
<NiN2N4	102.03	102.09	102.00	102.01	101.80	102.02	102.02
<NiN5N6	101.39	107.73	101.40	106.00	101.54	107.59	106.19
<NiO1C1	108.73	109.25	108.70	108.70	109.37	109.32	108.82
<NiO2C2	108.82	108.78	108.85	108.00	107.88	108.80	108.08
<NiO3C3	108.33	105.53	108.37	108.88	107.70	103.79	109.03

Figure 3. Torsion curves of un-substituted, *ortho*, *meta* and *para*-methyl Ni[C₆H₇CON₂]₃²⁺.

Figure 4. Torsion curves of un-substituted, *ortho*, *meta* and *para*-methoxyl $\text{Ni}[\text{C}_6\text{H}_7\text{CON}_2]_3^{2+}$.

Figure 5. Torsion curves of un-substituted, *ortho*, *meta* and *para*-methyl $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$.

Figure 6. Torsion curves of un-substituted, *ortho*, *meta* and *para*-methyl $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$.

In $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$, the energy barrier experienced on torsion is similar for methyl substituted except in *ortho* methyl substituted in which barrier height experienced is about 5.0 kcal/mol (Figure 5). The torsion curves of methoxyl substituted Cu(II) complex ions are quite similar to that of methoxyl substituted Ni(II) complex ions (Figure 6). It is very interesting to note that the curves for *ortho* and *para* methoxyl substituted Cu(II) complexes intercept at 50° and 135° - 144° , this could suggest that both complex ions can co-exist and react in very similar ways in solution under certain conditions. In general, methoxyl group contribution more to the geometry distortion than methyl substituted in both Ni(II) and Cu(II) complexes ions.

Evolution of HOMO and LUMO

Figure 7, 8, 9 and 10 show the evolution of the HOMO-LUMO energy difference (Δ) of the two series of substituted $\text{Ni}[\text{C}_6\text{H}_7\text{CON}_2]_3^{2+}$ and $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$ as a function of torsion angles. As expected, the change in torsion in the complexes affect π -electrons delocalization (complexes containing π -electrons system) and consequently affect the Δ gap which is a measure of electronic properties of the complexes. It is observed that changes in Δ become prominent with increase in torsion angles.

In $\text{Ni}[\text{C}_6\text{H}_7\text{CON}_2]_3^{2+}$, there is a decrease in Δ as the torsion angles become larger until 100° for the un-substituted and substituted except for *m*- CH_3 and *p*- OCH_3 substituted in which the Δ increases (Figure 7 and 8). The increment in torsion increased the electronic donating effect to the π -electrons delocalization of the benzoic rings except in *m*- CH_3 and *p*- OCH_3 substituted.

Figure 7. Evolution of HOMO-LUMO energy difference as a function of torsion angles for un-substituted, *ortho*, *meta* and *para*-methyl $\text{Ni}[\text{C}_6\text{H}_7\text{CON}_2]_3^{2+}$.

Figure 8. Evolution of HOMO-LUMO energy difference as a function of torsion angles for un-substituted, *ortho*, *meta* and *para*-methoxyl $\text{Ni}[\text{C}_6\text{H}_7\text{CON}_2]_3^{2+}$.

However, in the case of un-substituted and methyl substituted $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$, the curves are quite similar to that of $\text{Ni}[\text{C}_6\text{H}_7\text{CON}_2]_3^{2+}$ in that there is a decrease in Δ gap as the torsion angles become larger in un-substituted and *ortho*-methyl substituted (Figure 9). In Figure 10, methoxyl substituent has the same effect on the π -electrons delocalization of benzoic rings in the Cu(II) complexes. Calculated Mulliken charges on copper and Nickel atoms are $-0.494 \sim -0.351$ and $-0.974 \sim -1.061$ respectively. The charge on copper atom increases on addition of methyl and methoxyl substituents, the effect is more pronounced with methoxyl substituent especially on *meta* and *para* positions. However, *o*-OCH₃ substituent has little effect on atomic charge of copper which may due to formation of hydrogen bond. The atomic charge on nickel reduces slightly except *o*-OCH₃ substituted which increased.

Figure 9. Evolution of HOMO-LUMO energy difference as a function of torsion angles for un-substituted, *ortho*, *meta* and *para*-methyl $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$.

Figure 10. Evolution of HOMO-LUMO energy difference as a function of torsion angles for un-substituted, *ortho*, *meta* and *para*-methoxyl $\text{Cu}[\text{C}_6\text{H}_7\text{CON}_2]_2^{2+}$.

Conclusion

In order to investigate the electronic effects and geometrical distortions of methyl and methoxyl substituted Cu(II) and Ni(II) hydrazides ions, we have utilized the PM3 method. The relative stability of methoxyl substituted may be due to the formation of Hydrogen bonds between methoxyl oxygen and hydrogen on hydrazide ($\text{CH}_3\text{O} \cdots \text{HNNH}$; 1.817 Å for Cu(II) and 1.806–1.839 Å for Ni(II)). Methoxyl substitution has more noticeable effect on the complex ions than methyl substituted which may be due to internal rotations in methoxyl substituted ones.

The curves for *ortho* and *para* methoxyl substituted Cu(II) complexes intercept at 50° and 135° – 144° , this could suggest that both complex ions can co-exist and react in very similar ways in solution under certain conditions. In addition, both methyl and methoxyl substituents affect molecular stability of Cu(II) and Ni(II) hydrazides complex ions which is good indication that electronic properties control chemical reactivity.

References

1. Odunola O A, Adeoye I O and Woods J A.O, *Synth React Inorg Met Org Chem.*, 2002, **32(4)**, 801-817.
2. Odunola O A, Adeoye I O and Woods J A O and Gelebe A C, *Synth React Inorg Met Org Chem.*, 2002, **33(2)**, 205-221.
3. Ranganathan D, Vaish N K, Shah K, Roy R, Madhusudanan K.P, *J Chem Soc Chem Commun.*, 1993, 92.
4. Karle I, Ranganathan D, Shah K and Vaish N K, *Int J Pept Protein Res.*, 1994, **43**, 160.
5. Rosen M K, Standaert R F, Gaalat A, Nakatsuka M, Schreiber S.L, *Science*, 1990, **248**, 863.
6. Chatani Y, Ueda Y, Tadokoro H, Deits W and Vogt O, *Macromolecules*, 1978, **11**, 636-638.
7. Gaymans R.J, Ventatraman V S and Schuijjer J, *J Polym Sci., Polym Chem Ed.*, 1984, **22**, 1373.
8. Franco L, Subirana J A and Puiggali J, *Macromolecules*, 1998, **31**, 3912.

9. Frazier A H and Wallenberg F T, *J Polym Sci.*, Part A, 1994, **2**, 1147.
10. Aleman C, Lotz B and Puiggali J, *J Molecular Structure(Theochem)*, 2001, 541,179-183
11. Aleman C and Puiggali J, *J Org Chem.*, 1999, **64**, 351.
12. Jamieson E.R and Lippard S.,*J Chem Rev.*, 1999, **99**, 2467-2498.
13. Gielen M, Biesemans M, de Vos D and Willens R J, *Inorg Biochem.*, 2000,**79**, 139-145.
14. Henry C Wojciech and Pruchnik F J, *Int J Mol Sci.*, 2001, **2**, 148-155.
15. Spartan Essential 2.0.1, Wavefunction, Inc., Irvine 2005.
16. Kong C A, White A I, Krylov C D, Sharill R D, Adamon T R, Furlani M S, Lee A M, Lee S R, Gwaltney T R, Adams C, Ochsenfeld A T B, Gidert G S, Krddziora V A, Rassolov D R, Maurice N, Nair Y, Shao N A, Bashey P E, Maslen J P, Domobroski H, Daschil W, Zhang P P, Korambath J, Baker E F C, Byrd T, Van V A, Oumi S, Hirata C P, Hsu N, Ishikawa T, Florion A, Warshet B G, Johnson P M W, Gui M, Head-Gordon, Pople J A, *J Comput Chem.*, 2000, **21**, 1532.
17. Hehre W J, Wavefunction, Inc. Irvine, USA 2003.